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Mapping Analyte Distributions in Surrogate Nuclear Melt Glass Using Laser-Induced Breakdown Spectroscopy and Micro X-Ray Fluorescence

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Outline

- Research Goals and Approach
- Motivation and Background
- Surrogate Melt Glass Production
- X-ray/Gamma Spectroscopy Comparison
- Micro-XRF Initial Results
- Laser Induced Breakdown Spectroscopy (LIBS) Initial Results
- Conclusions
- Path Forward

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Research Goals:

- Explore feasibility of portable LIBS and micro-XRF systems as methods of field screening for real debris
- Develop a LIBS Capability to rapidly screen beads for production quality control
- Complete 3D elemental mapping of surrogate debris to determine uranium and other elemental migration patterns during debris formation

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Scientific Approach:

- Produce melt glass “test sets” which isolate individual analytes
- Use portable COTS LIBS systems for line identification and field use
  - “Insight” benchtop LIBS by Photon Machines (Y12)
    - Nd:YAG, 266 nm, 80 mJ/pulse, 8 ns pulse width, Ocean Optics LIBS 2500 spectrometer
  - Z500-ER handheld LIBS by SciAps (Y12)
    - Nd:YAG, 1064 nm, 5 mJ/pulse, 1 ns pulse width, internal spectrometer
- Use traditional LIBS laboratory set up and physical sample sectioning for elemental mapping (UT MABE)
  - Nd:YAG, 355nm, 10ns pulse width, 80 mJ/pulse laser Princeton SpectraPro 2300i Spectrometer
- Compare results with COTS, portable Micro-XRF mapping of the same beads
  - Bruker M4 Tornado Micro-XRF (LANL)

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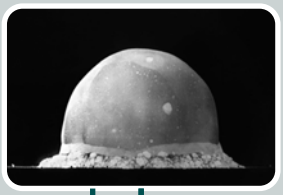
Melt Glass Background

Nuclear Event



Type of Burst

- Environmental Analysis

Matrix Formation

Analysis Process

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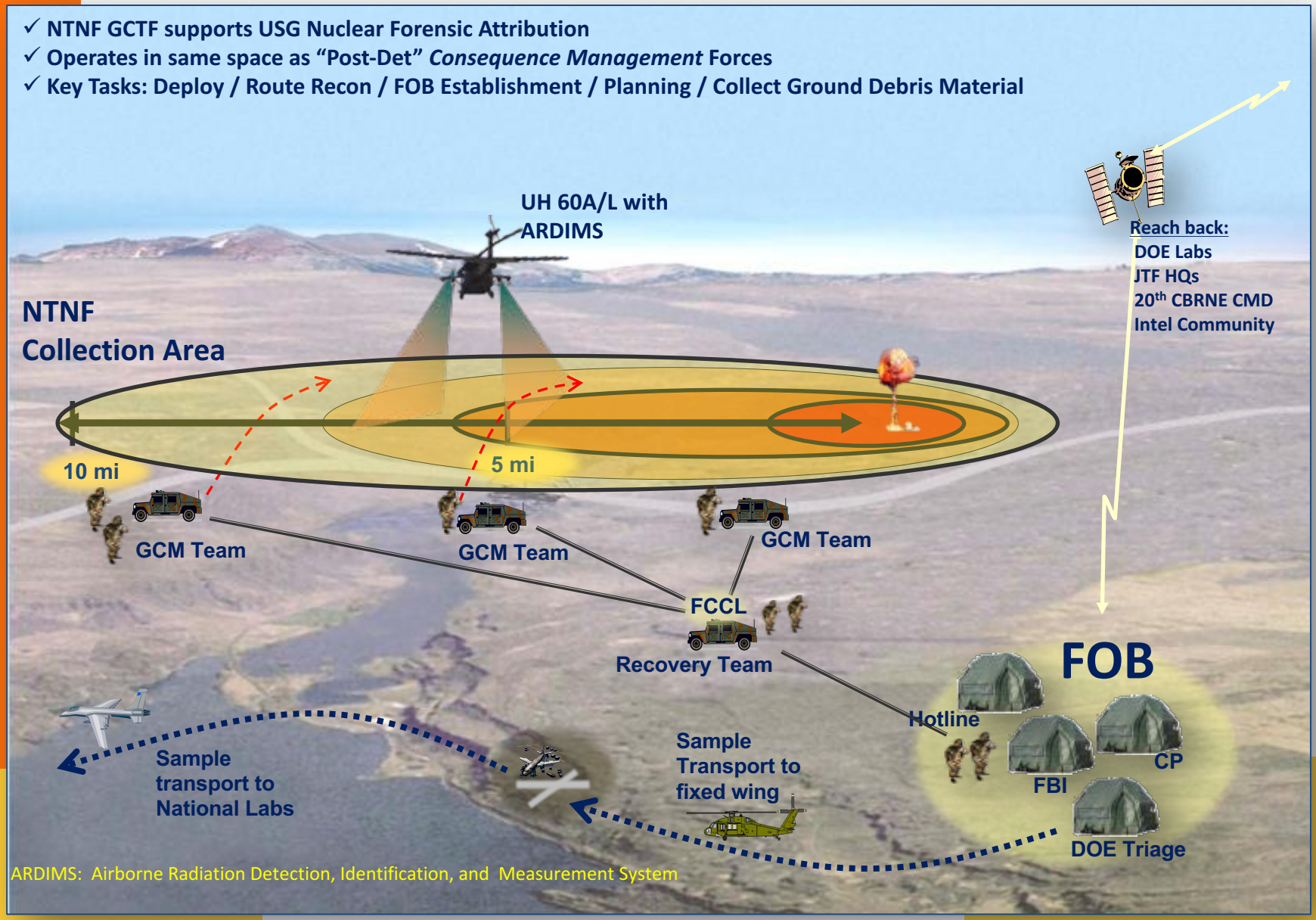
NTNF GCTF Tactical CONOP

- ✓ NTNF GCTF supports USG Nuclear Forensic Attribution
- ✓ Operates in same space as "Post-Det" *Consequence Management* Forces
- ✓ Key Tasks: Deploy / Route Recon / FOB Establishment / Planning / Collect Ground Debris Material



ARDIMS: Airborne Radiation Detection, Identification, and Measurement System

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UT Surrogate Debris Formulas

- Synthetic Testable Urban Formulation for Forensics(STUFF)
  - Trinitite ; New York City; Houston
- Nuclear Under Ground Engineered Test Surrogates (NUGETS)
- Marine Urban Debris (MUD)

Soil Composition from GZ

Building Composition

City Infrastructure

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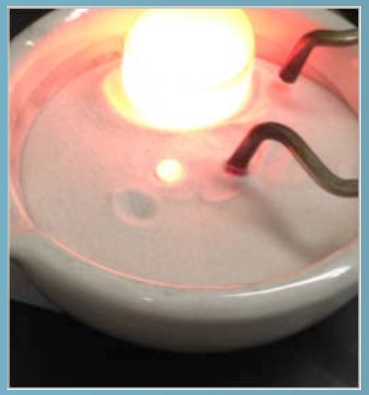
Synthesis Process



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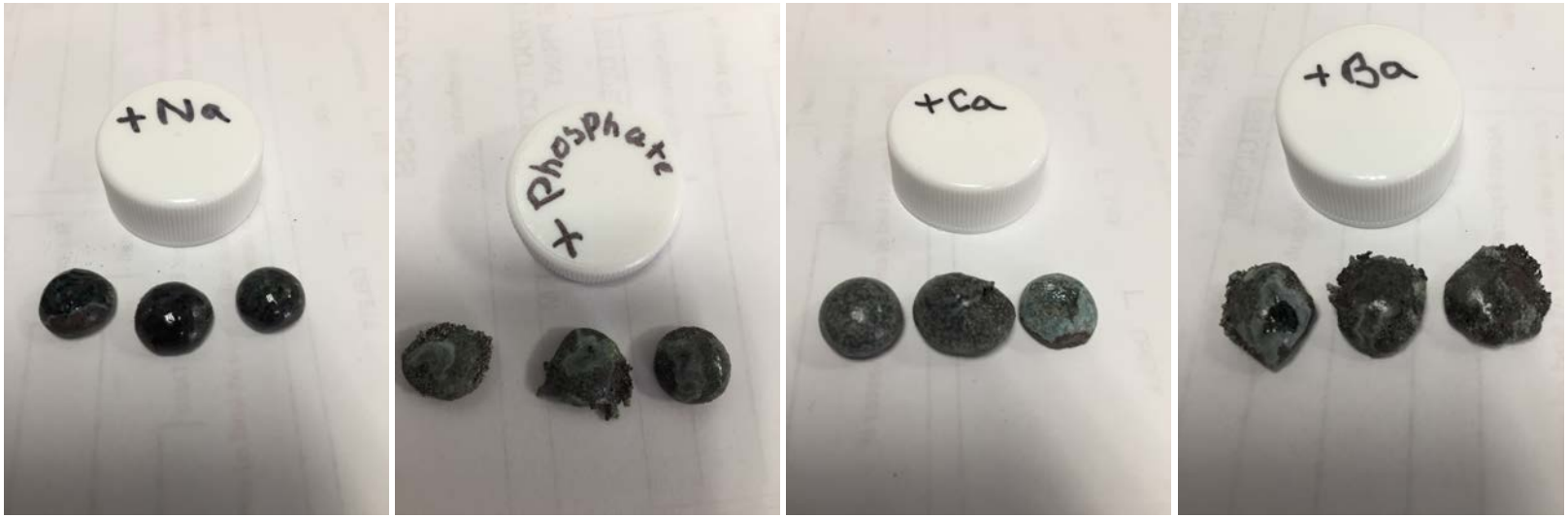
Inherent Variability in Morphology and Chemical Distributions



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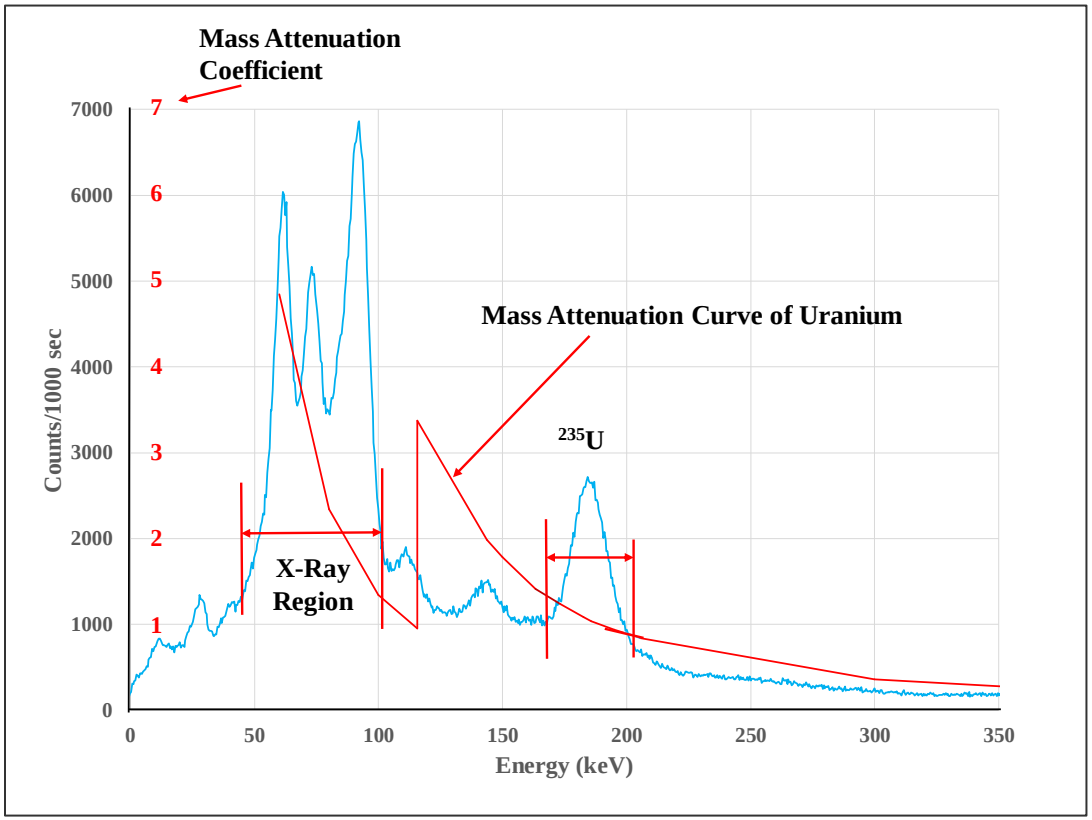
X-Rays and Gamma Rays as Signatures for Natural Uranium



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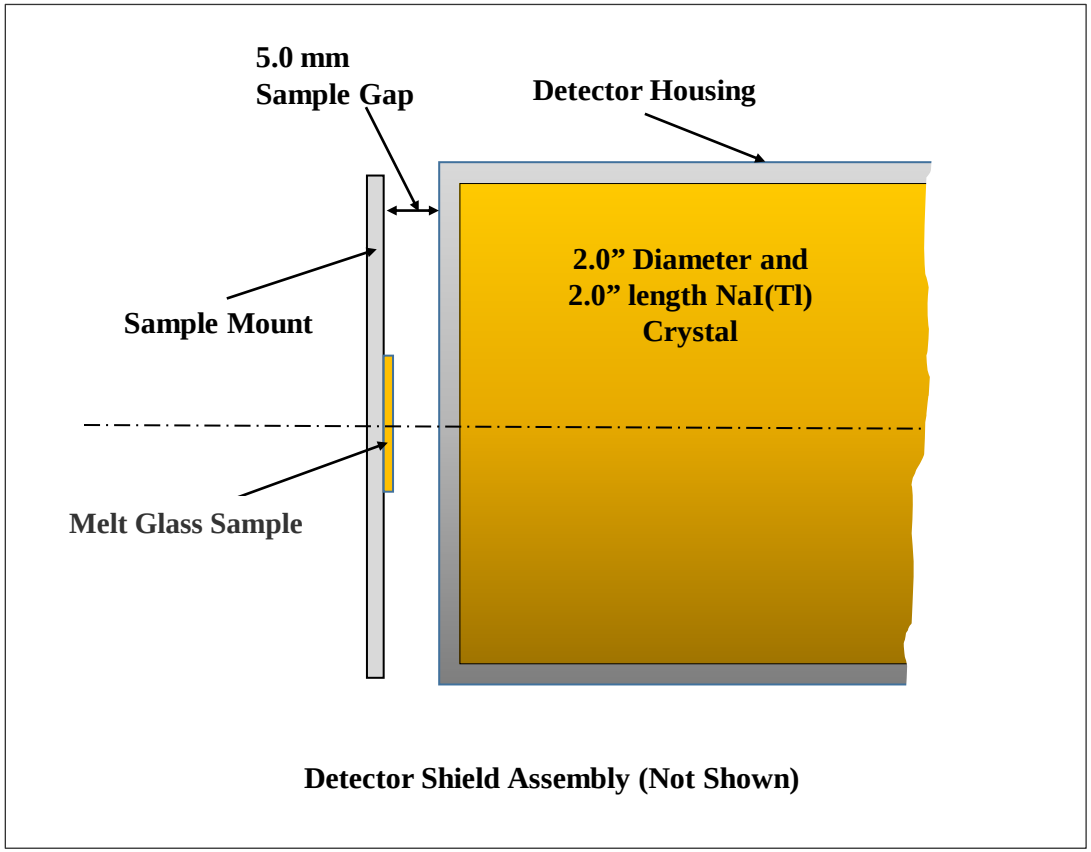
X-ray/Gamma-ray Experimental Setup



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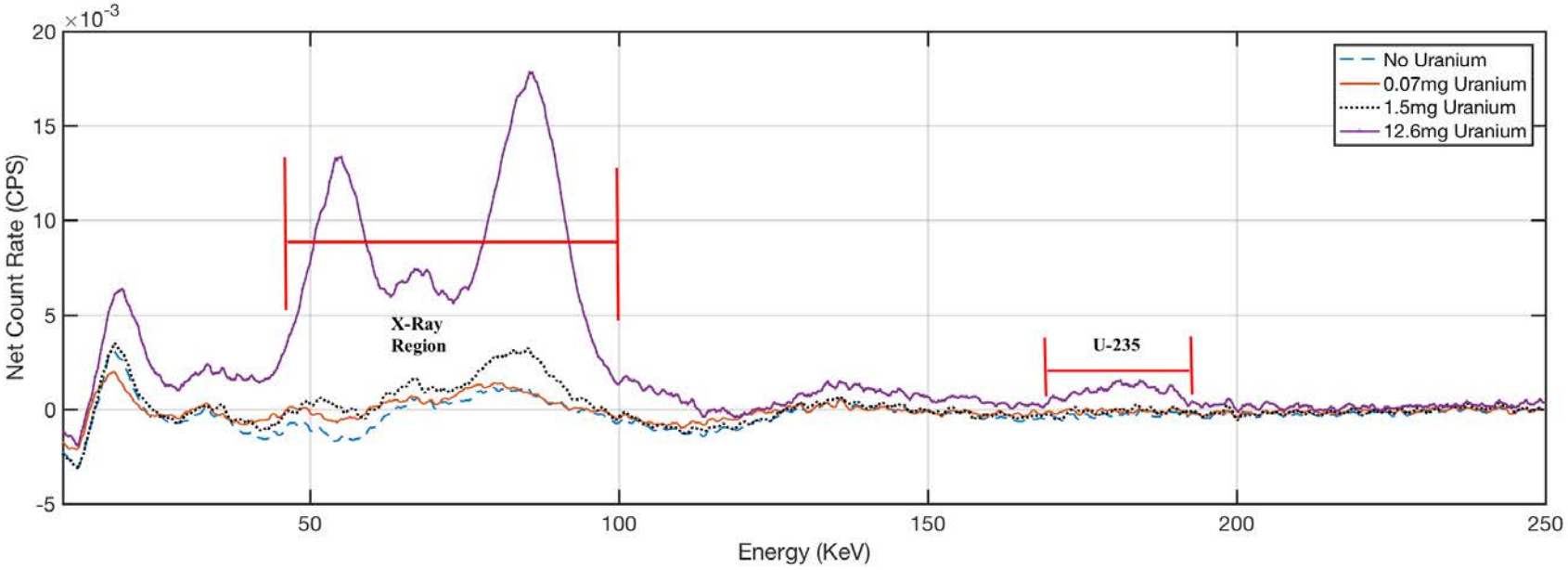
Melt Glass X-Ray/Gamma Spectrum



- Confirmation of the presence of uranium
- Long dwell time required
- No local concentration

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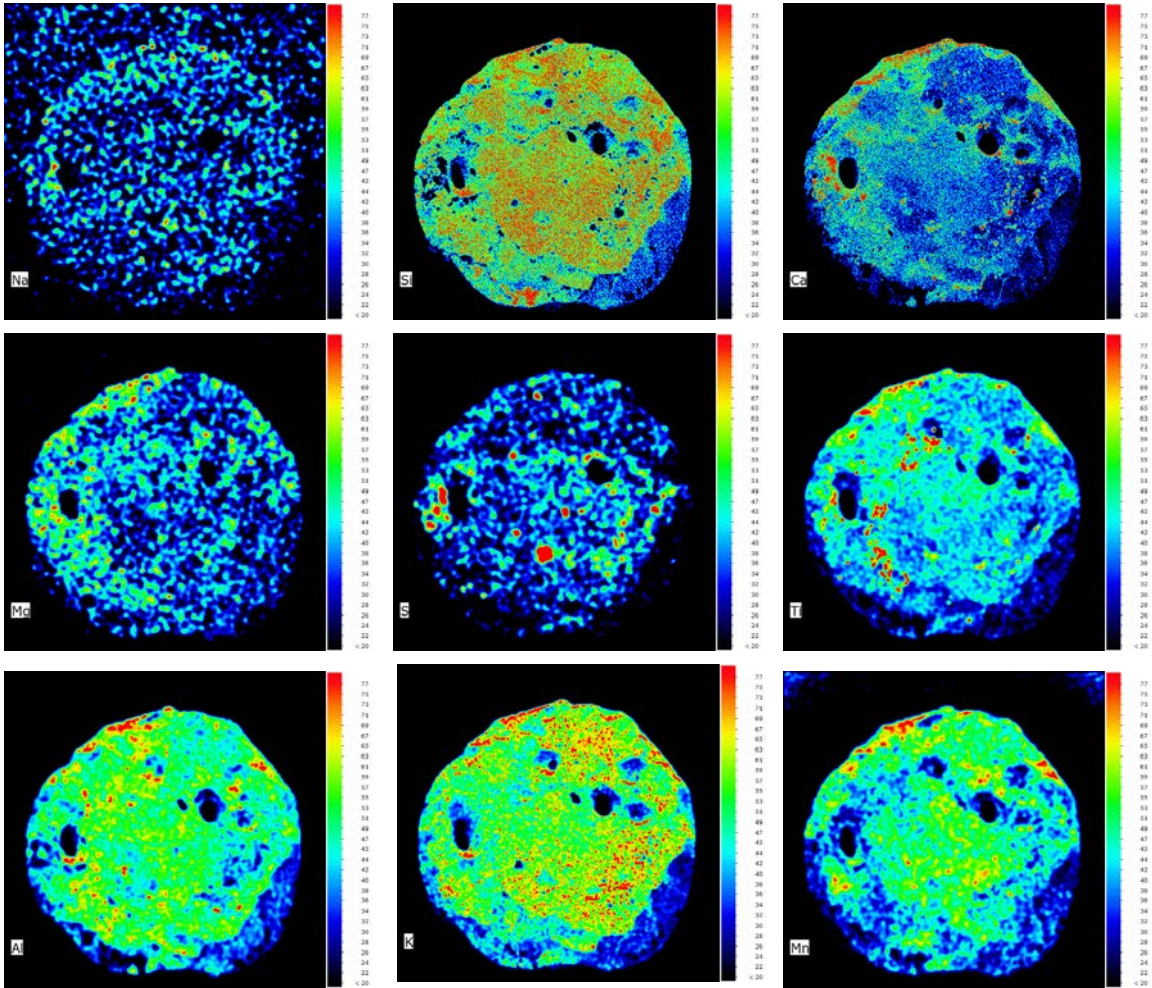
Initial LANL Micro-XRF mapping confirms chemical heterogeneity (1 of 2)



kmb1625003

40 kV, 500 µA
20 µm spot
20 µm distance
1 ms/pixel = 15 min

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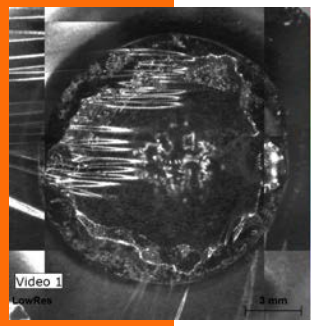
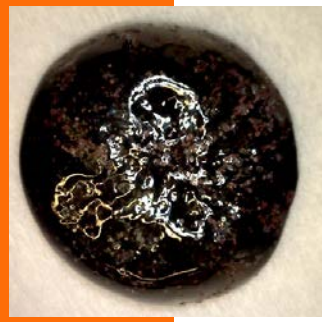
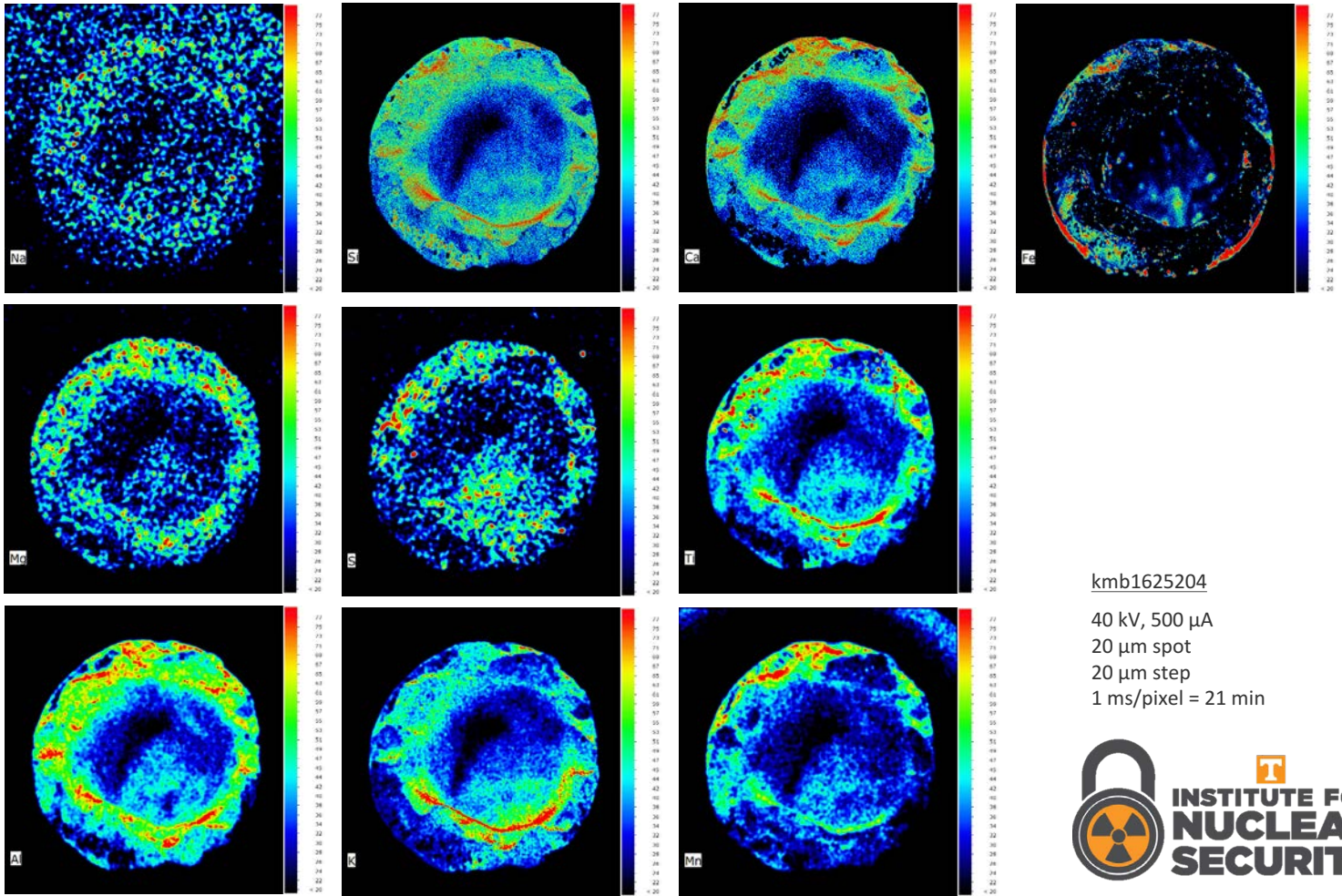
Initial LANL Micro-XRF mapping confirms chemical heterogeneity (2 of 2)







kmb1625204

40 kV, 500 µA
20 µm spot
20 µm step
1 ms/pixel = 21 min

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Melt glass production for specific LIBS line identification

Melt Glass Bead Ingredients for Line Identification	
NYC Recipe	Nominal %
SiO2	60.48
NaO	3.23
Fe2O3	7.63
Al2O3	15.10
CaO	6.35
KOH	3.55
MgO	2.65
S	0.06
BaO	0.06
MnO	0.12
Ca3(PO4)2	0.10
TiO	0.61
UNH	0.06
Total	100.00

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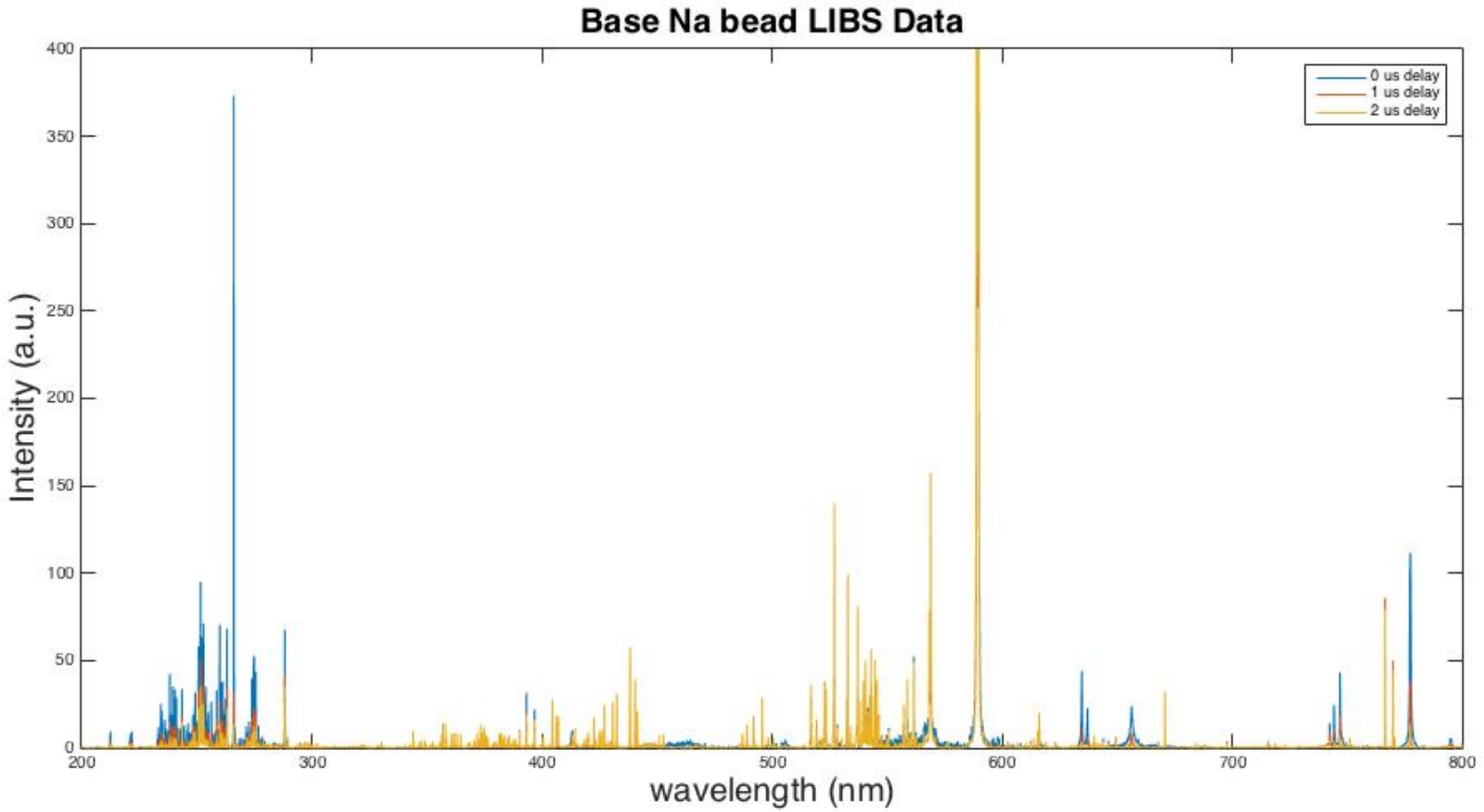
Broadband LIBS Spectrum to identify interference free lines



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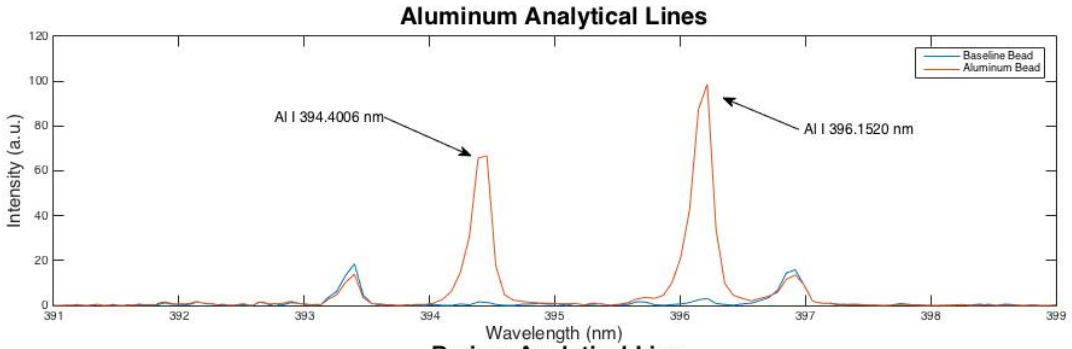
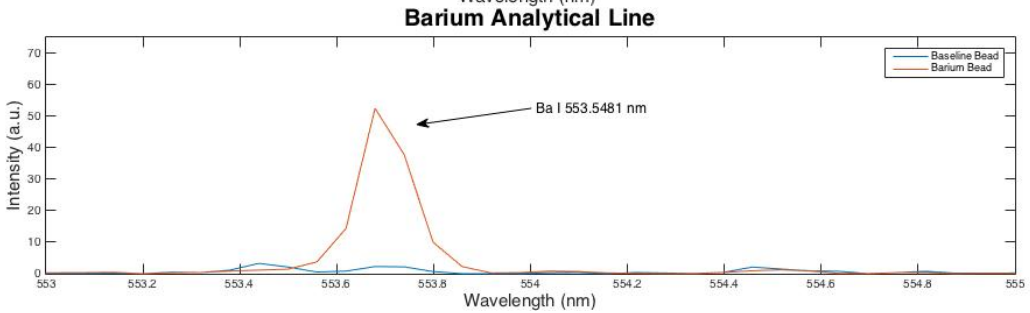
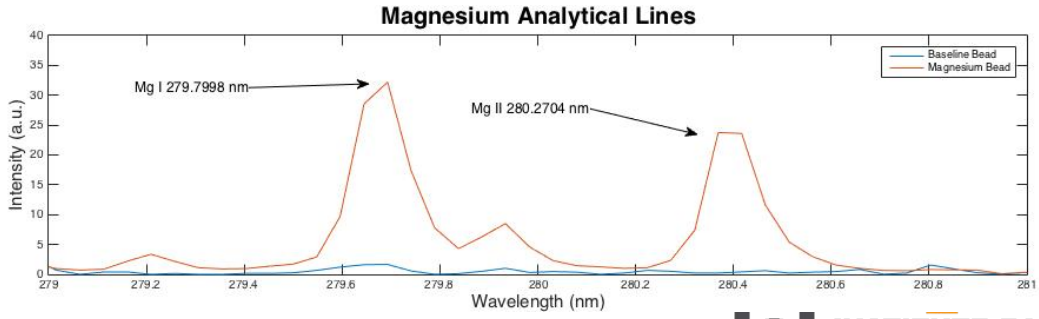
Analytical lines for non-radioactive elements

Analytical Lines Selected

Peak (nm)	Source	A (s^-1)	Eu (eV)	g
248.327	Fe I	4.80E+08	4.9913	11
279.800	Mg I	4.79E+08	8.8637	6
280.270	Mg II	2.57E+08	4.4224	2
288.158	Si I	2.17E+08	5.0823	3
328.560	Na II	1.10E+08	37.0948	5
373.486	Fe I	9.01E+07	4.1777	11
394.401	Al I	4.99E+07	4.1427	2
396.152	Al I	9.85E+07	3.1427	2
403.076	Mn I	1.70E+07	3.0751	8
440.475	Fe I	2.75E+07	4.3714	9
453.478	Ti I	6.87E+07	3.5693	9
453.557	Ti I	lot Available	3.5587	7
455.403	Ba I	1.18E+08	2.7218	4
521.262	S I	8.47E+07	17.4457	6
542.999	Fe I	6.00E+07	12.8787	10
553.548	Ba I	1.19E+08	2.2392	3
561.863	Fe I	2.24E+06	6.4149	5
585.745	Ca I	6.60E+07	5.0486	5
588.995	Na I	6.16E+07	2.1044	4
616.217	Ca I	4.77E+07	3.9104	3
656.279	H I	4.41e+07	12.0875	18
766.429	Fe I	3.37E+05	4.6076	7
766.490	K I	3.80E+07	1.6171	4
769.897	K I	3.75E+07	1.6100	2







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Uranium line identification via SciAps Z500-ER Handheld LIBS

Enhanced Uranium Content Beads	
UNH Mass	**Nominal %**
NYC (7.2 mg)	0.06%
12.6 mg	0.11%
50.0 mg	0.42%
500.0 mg	4.17%

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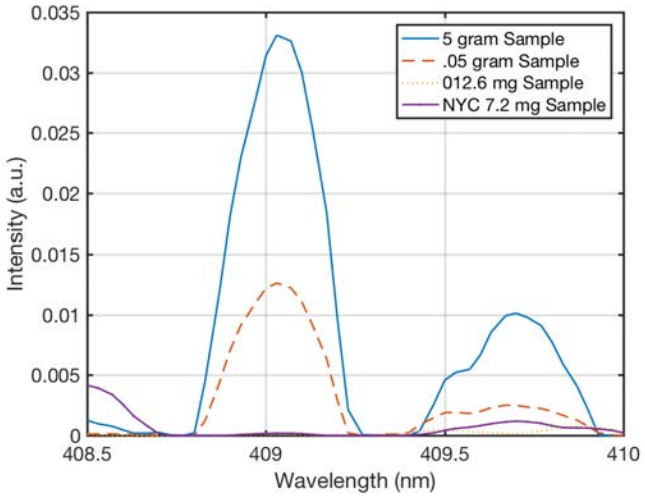
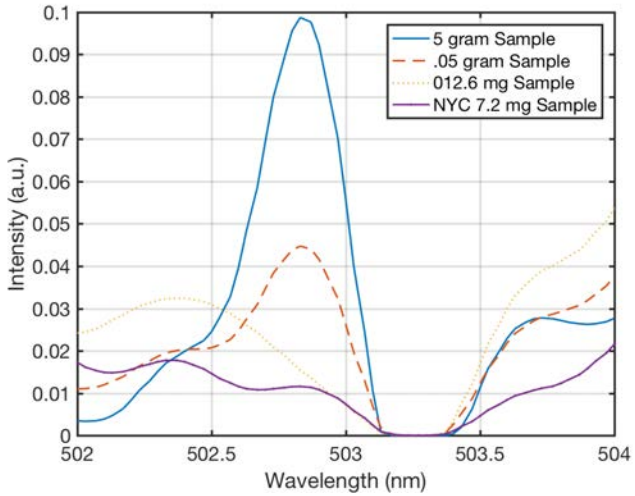
Uranium Line Identification

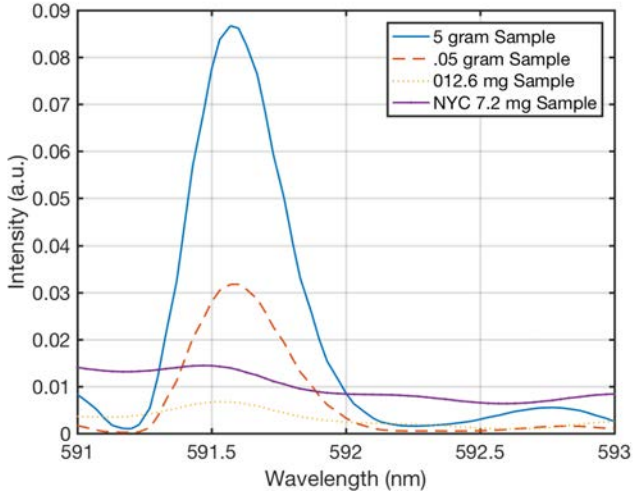
U(II) 409.013 nm



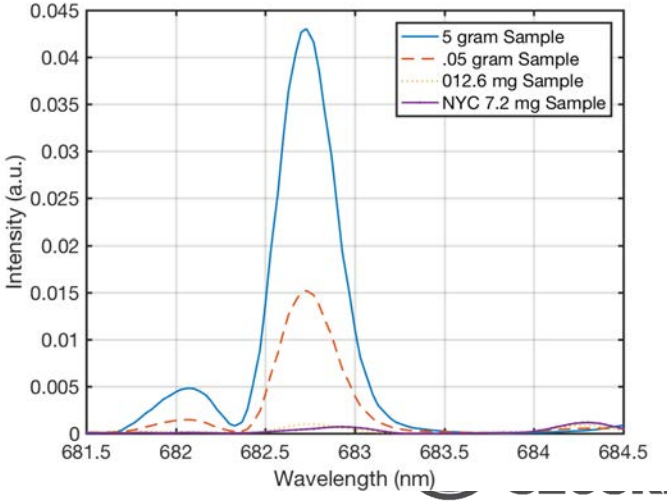
U(I) 502.738 nm



U(I) 591.539 nm



U(I) 682.691 nm



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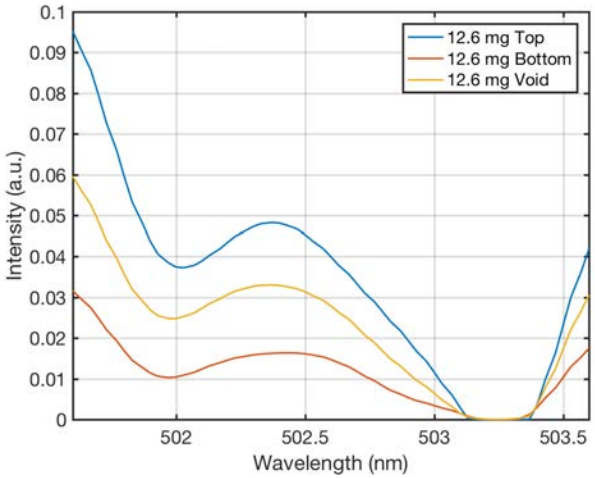
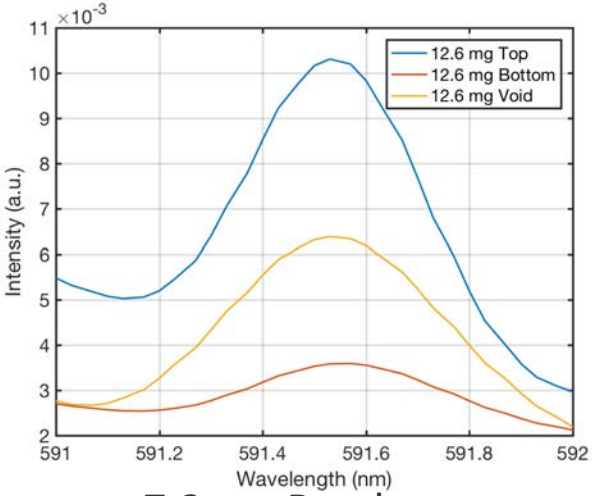
Uranium Content Variation

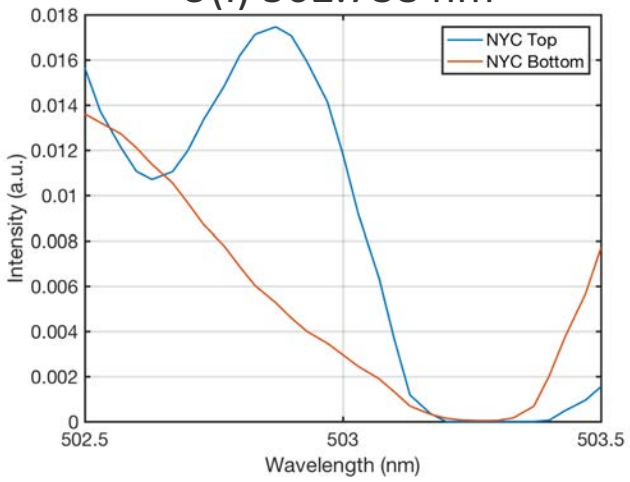
12.6 mg Bead
U(I) 502.738 nm



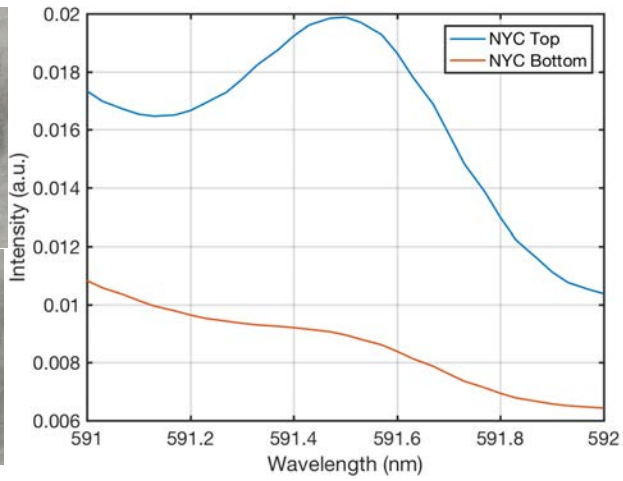
12.6 mg Bead
U(I) 591.539 nm



7.2 mg Bead
U(I) 502.738 nm



7.2 mg Bead
U(I) 591.539 nm



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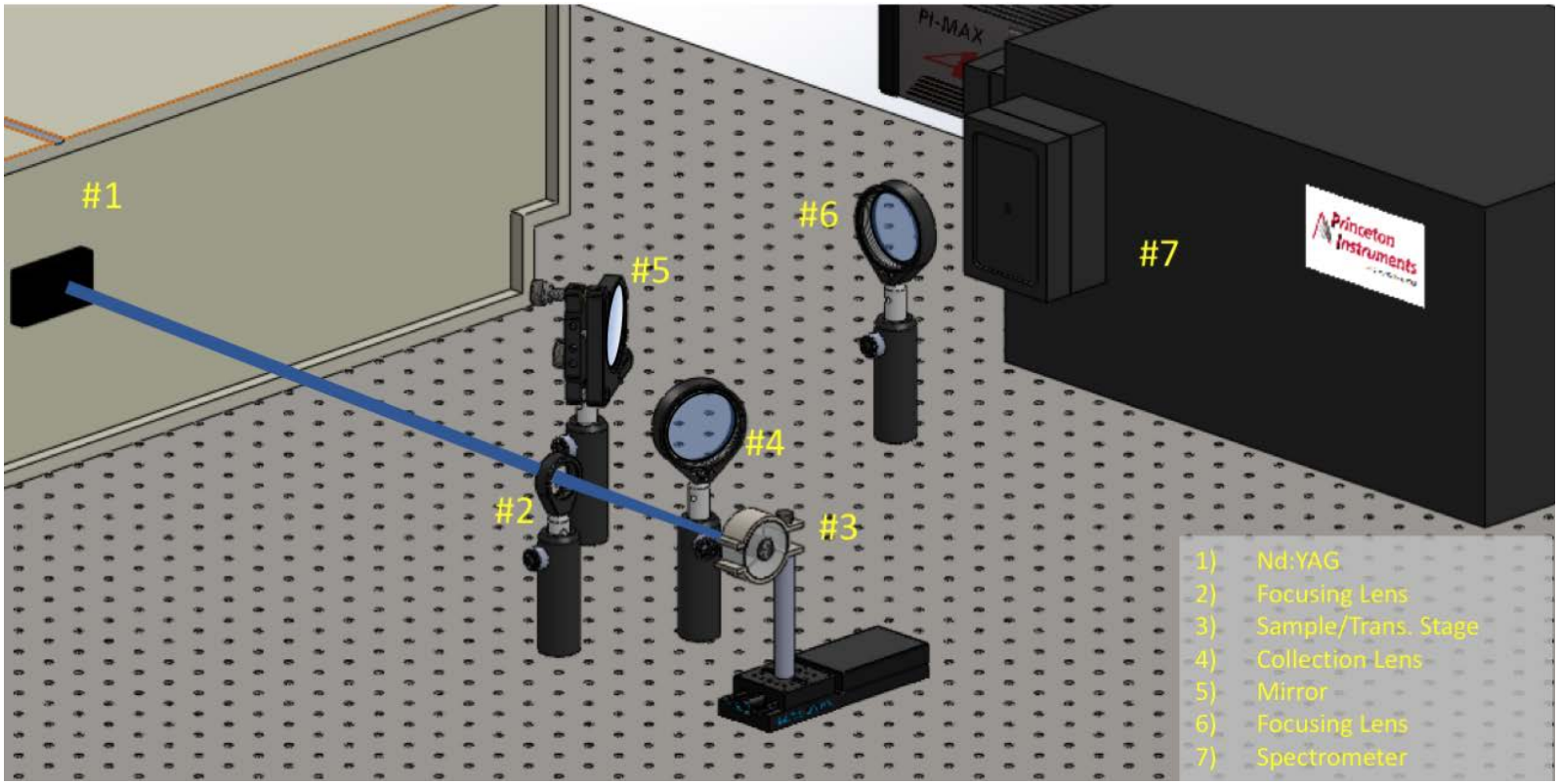
Experimental Setup for Chemical Mapping



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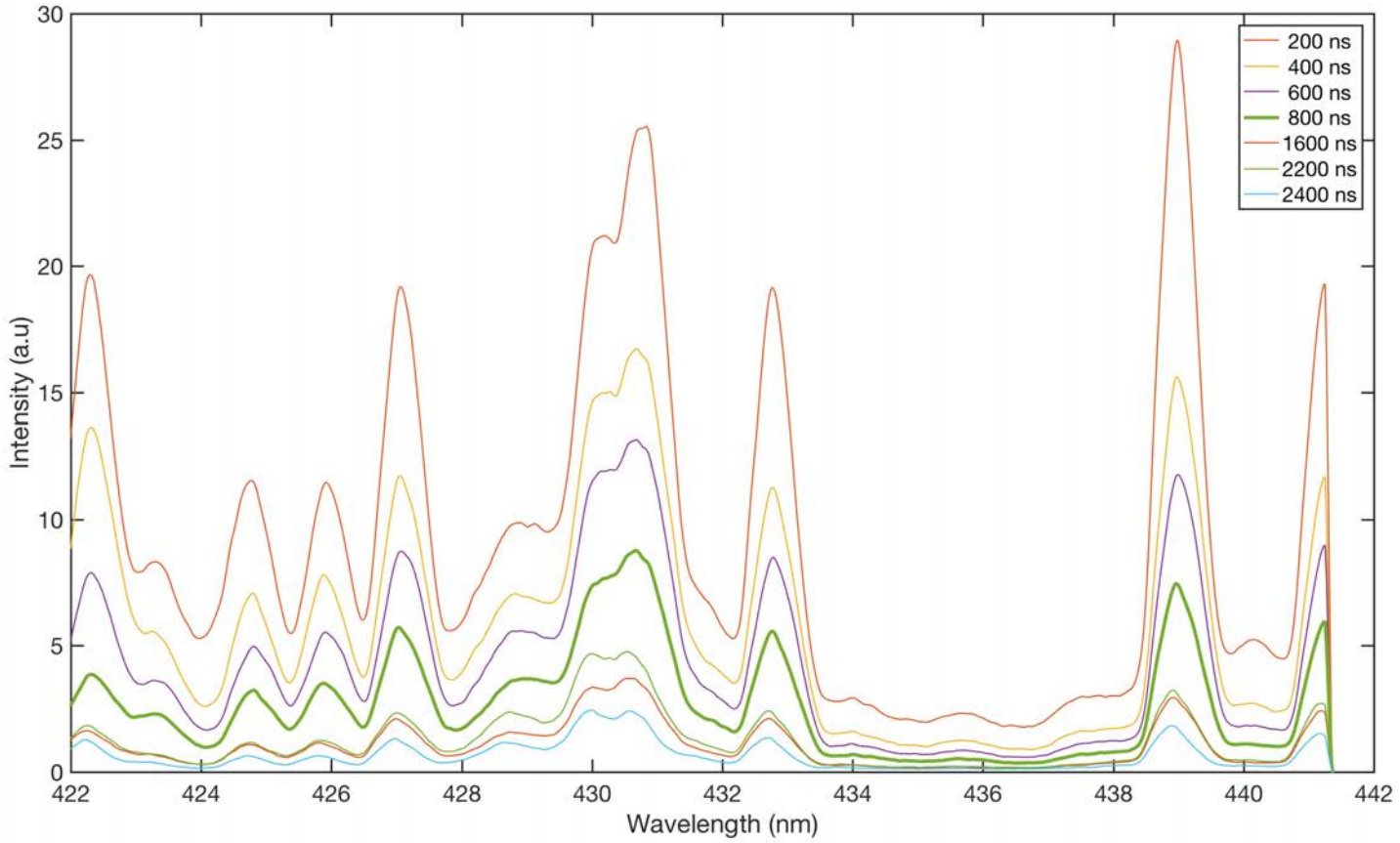
Time Delay and Gate Optimization



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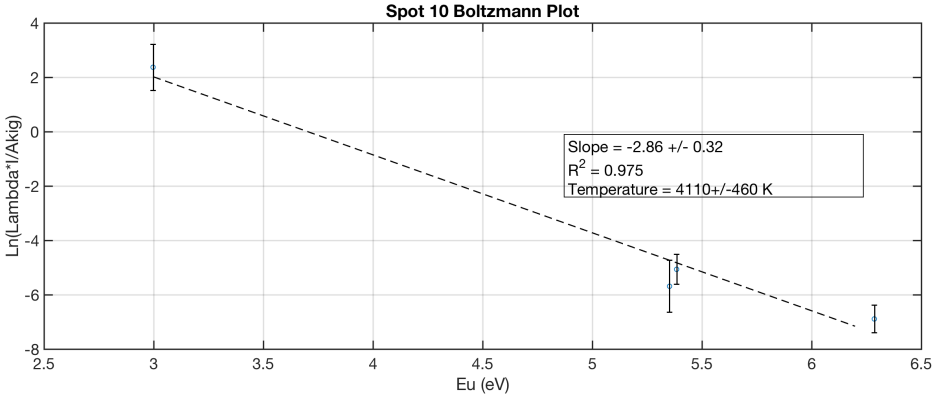
Four Fe Lines Chosen for Analysis; One Line of Spots Ablated



Lines Used for Iron Mapping			
Source	**Wavelength (nm)**	**Akig (s^-1)**	**Eu (eV)**
Fe (I)	422.22128	4.03E+07	5.3852074
Fe (I)	424.74253	2.13E+08	6.2864786
Fe (I)	425.83156	1.78E+04	2.9980448
Fe (I)	427.11535	1.64E+08	5.3515703

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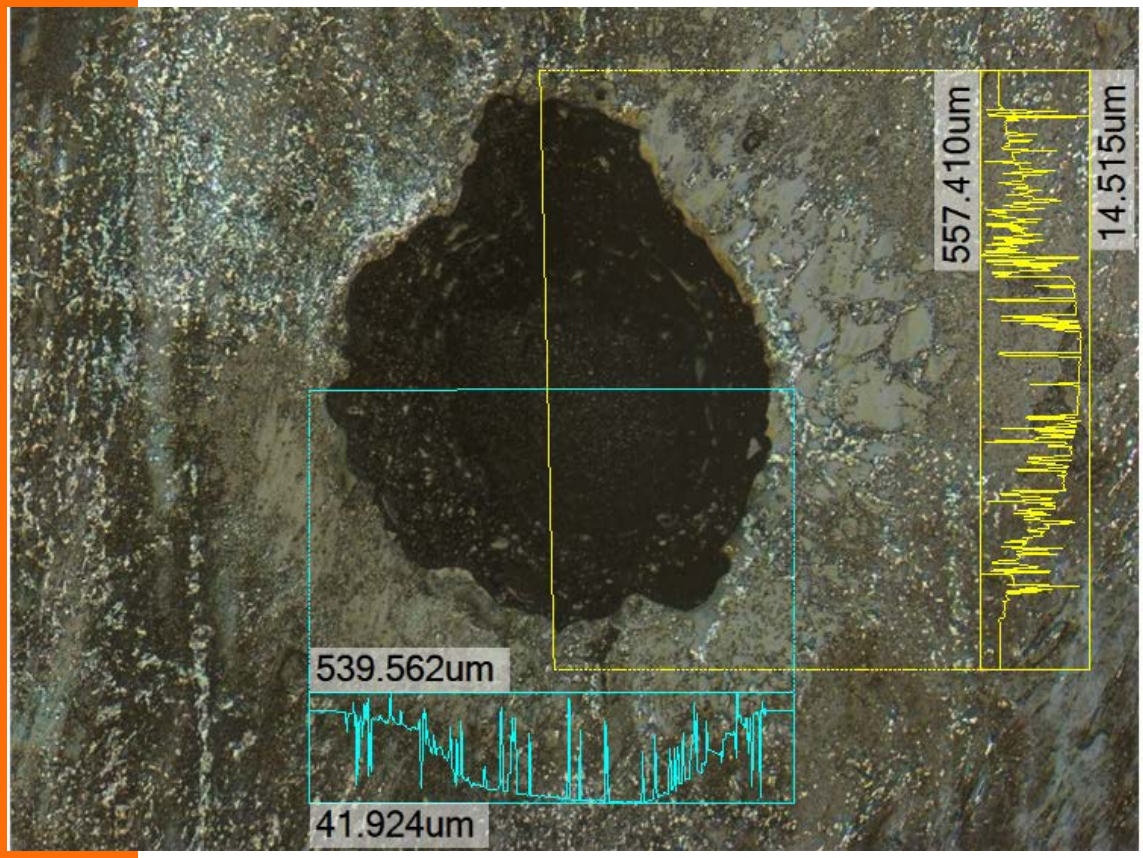
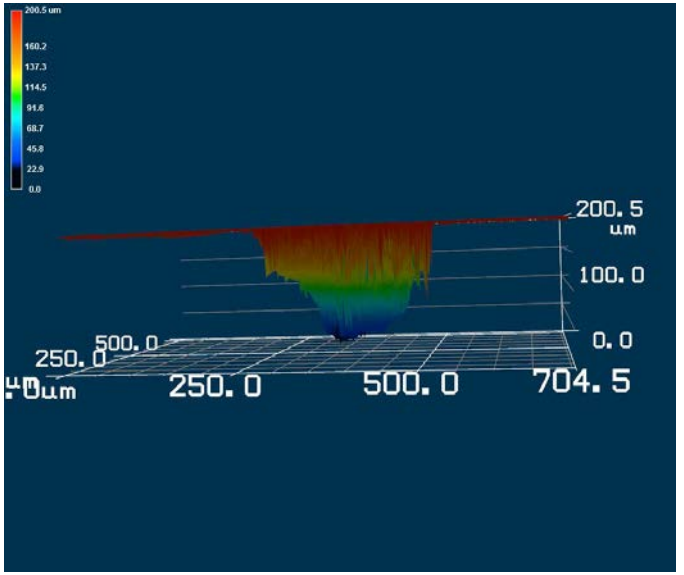
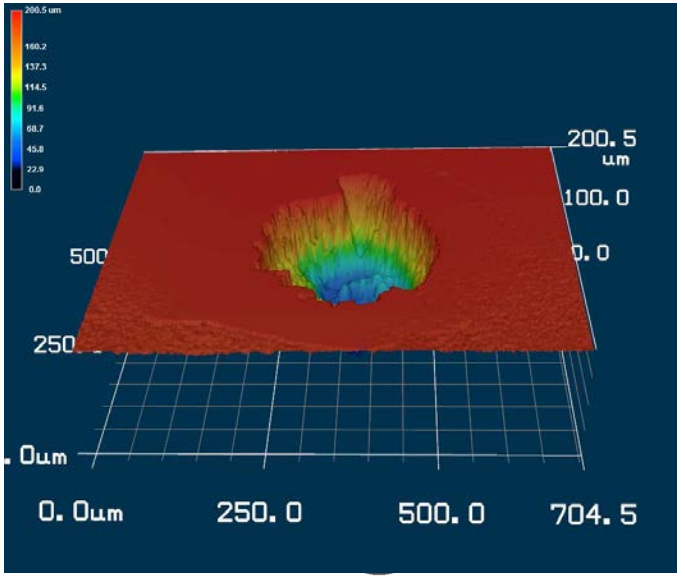
50 pulses per location







Ablation Craters

- diameter: 290-300 µm
- Depth: 300-500 µm

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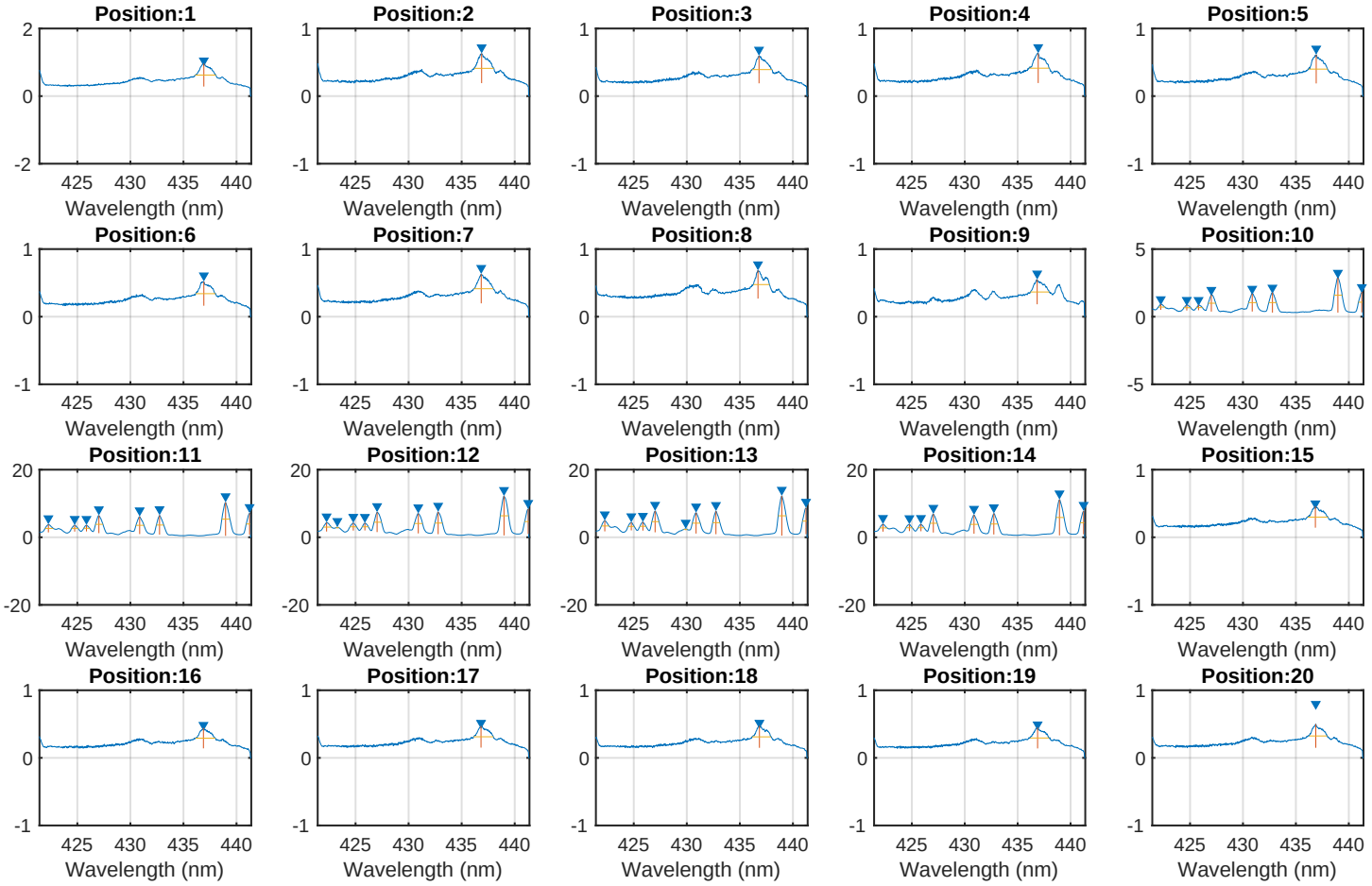
Positions 10-14 Provide Sample Information



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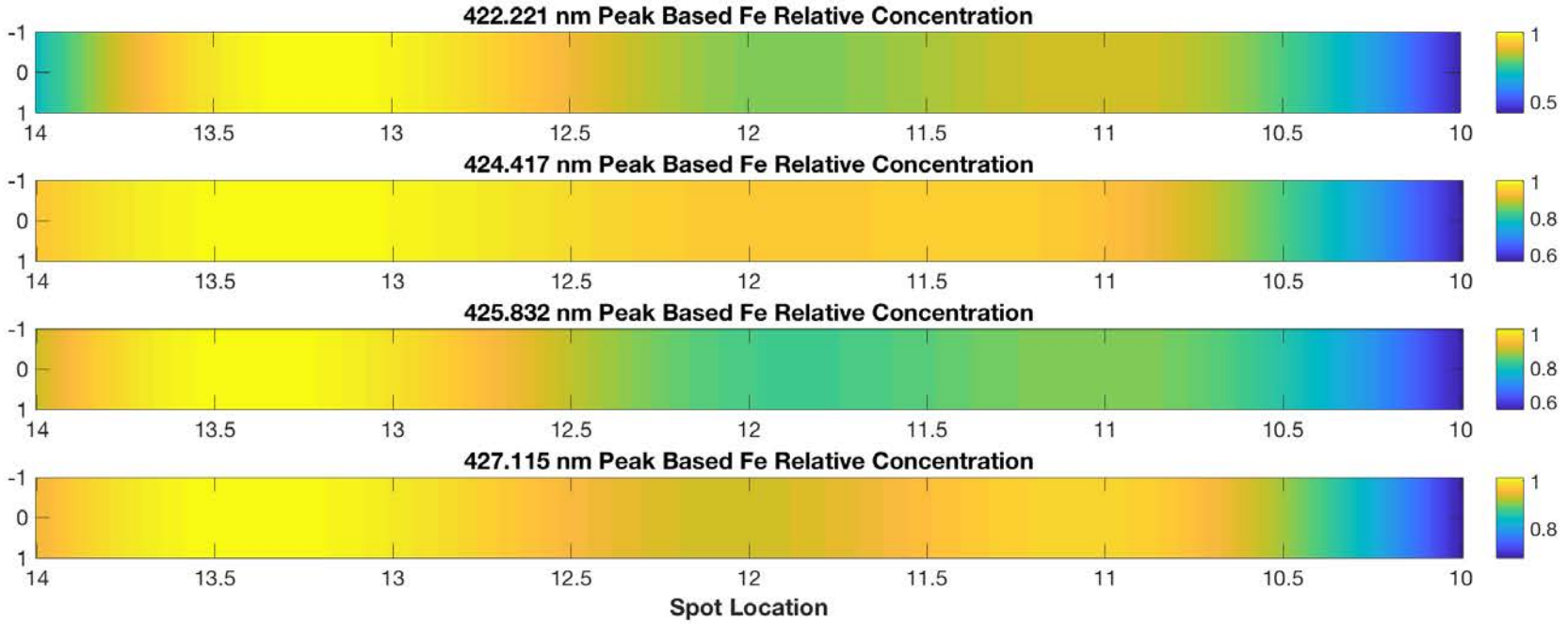
Fe concentrations via peak ratios show self consistency



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Conclusions

- Micro-XRF and LIBS both have the capability to map analytes in melt glass production
- Both have COTS instruments that could be used in a forward deployed environment
- The complex nature of the sample presents challenges to both techniques
- Multiple instruments may allow sample collectors greater confidence in the fidelity of their samples before shipment to offsite locations

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Next Steps

- Round Robin 2D Chemical Mapping with Micro-XRF and LIBS systems on a common sample set
- 3D mapping via physical sectioning
- Increase sample throughput to measure variability in the melt glass production process

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- Dr. Ashly Stowe (Y12)
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- Asia Conley (UTK)
- Jason Matheny (UTK)

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Thank You!

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